REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY *(Leave Blank)*	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	31 Mar 1998	Progress Report: 1 Jan 98 - 31 Mar 98

4. TITLE AND SUBTITLE
Nanocrystalline Processing and Interface Engineering of Nitrides

5. FUNDING NUMBERS
G - N00014-95-1-0626

6. AUTHORS
Jackie Y. Ying
Martin L. Panchula

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Department of Chemical Engineering
Massachusetts Institute of Technology
77 Massachusetts Avenue, Room 66-544
Cambridge, MA 02139-4307

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Office of Naval Research
800 North Quincy Street
Ballston Tower One
Arlington, VA 22217-5660

10. SPONSORING / MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION / AVAILABILITY STATEMENT

Approved for public release; distribution unlimited

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

This report describes preliminary results obtained from nitridation of nanocrystalline aluminum into nanocrystalline aluminum nitride. In comparison to commercial microcrystalline aluminum, the nanocrystalline aluminum displays significantly higher nitridation rates and does not require high temperatures to achieve significant conversion. Future research will examine the kinetics of the nitridation process and synthesizing nanocrystalline aluminum nitride directly in the forced flow reactor.

14. SUBJECT TERMS	15. NUMBER OF PAGES
Nanocrystalline, Nitridation, Aluminum, Aluminum Nitride	3
	16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	UL

"Nanocrystalline Processing and Interface Engineering of Si_3N_4-based Nanocomposites"

Technical Report on ONR Grant No. N00014-95-1-0626
for the period of January 1, 1998 - March 31, 1998

Jackie Y. Ying
Department of Chemical Engineering
Massachusetts Institute of Technology
Room 66-544, 77 Massachusetts Avenue
Cambridge, MA 02139-4307
Tel: (617) 253-2899
Fax: (617) 258-5766

Nanocrystalline Aluminum Synthesis and Nitridation

Recent efforts have been focused on the synthesis and nitridation of nanocrystalline aluminum in order to produce nanocrystalline aluminum nitride via direct nitridation[1]. Typically, temperatures in excess of 1000°C are necessary to complete nitridation of aluminum because of diffusional limitations. The nitridation of large aluminum particles may follow two different paths depending on the temperature of nitridation. The first step is the nitridation of a surface layer that acts as a barrier layer through which the reactants - either aluminum or nitrogen - must diffuse in order to complete the conversion. The next step in the process depends on the temperature of nitridation. Chang *et al.*[2] reported that at temperature below 1200°C the nitrogen diffuses through the AlN layer to react with the aluminum; while at temperatures greater than 1200°C the molten aluminum moves through cracks in the AlN surface and may even result in a hollow particle. The activation energy for the reaction reportedly changed from 1054 kJ/mole to 354 kJ/mole as the temperature was increased above 1200°C. The large increase in the kinetics of nitridation was attributed to the exposure of fresh aluminum surfaces, and a change in the rate limiting step from surface reaction to nitrogen diffusion.

It was initially expected that enhanced nitridation of the nanocrystalline aluminum would be possible and would be due primarily to the decrease in diffusional distances within the aluminum. However, the results obtained (Figure 1) appear to be difficult to explain on this basis alone, though additional quantitative analysis need to be completed. Figure 1 was obtained by nitriding aluminum samples in a Perkin Elmer TGA7 under a 50 cc/min purified grade 5 nitrogen stream. Each sample was purged for 2 hours prior to running the heating cycle in the thermal gravimetric analyzer. Oxygen content in the TGA is still several ppm based upon carbon tests run just prior to the aluminum nitridation. The nanocrystalline aluminum sample created in our forced flow reactor shows significantly more nitridation than does the large 20 μm commercial aluminum spheres. The theoretical nitridation reaction:

$$Al + \tfrac{1}{2} N_2 \rightarrow AlN \qquad (1)$$

should give a weight increase of 151.9%. While the nanocrystalline aluminum produced in our reactor attains approximately this value (153%) during the heat treatment, the commercial aluminum does not achieve any significant weight gain (1.7%). X-ray diffraction patterns of the starting nanocrystalline aluminum and the aluminum nitride created in the TGA are shown in Figure 2. The nanocrystalline aluminum was produced at 7 mbar of pressure and has a grain size of approximately 50 nm.

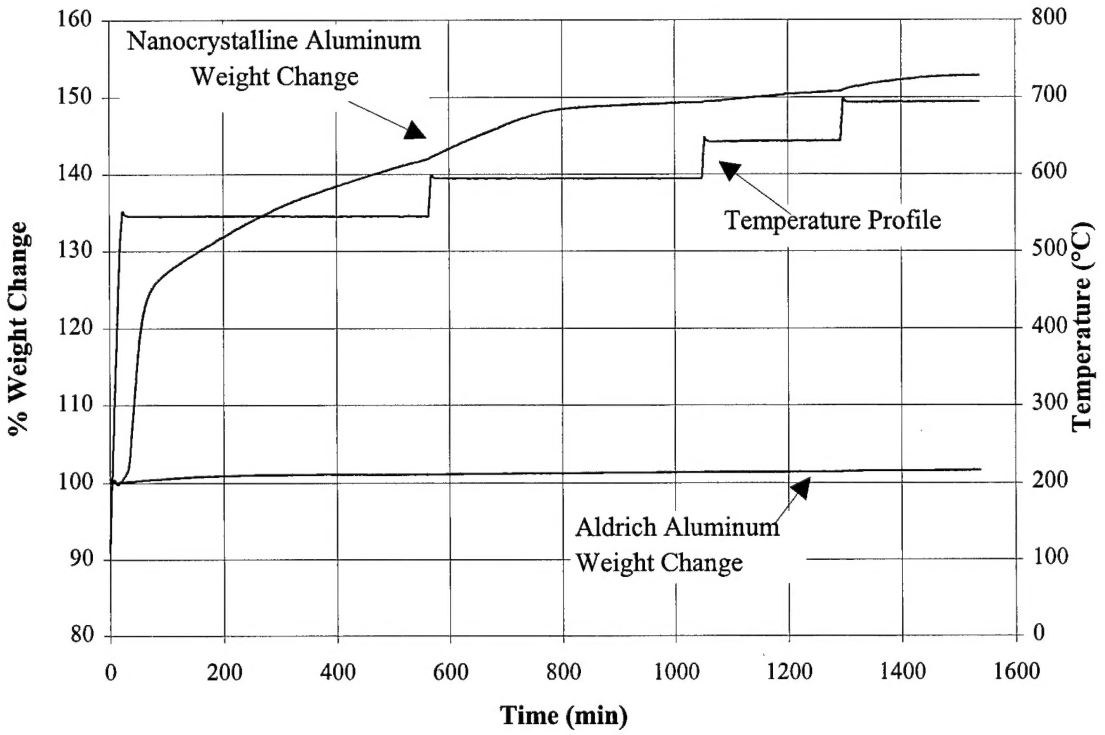

Figure 1. Weight change and heating profile for nitridation of nanocrystalline and microcrystalline aluminum.

The nitrided aluminum appears to be made up of three phases, AlN, γ-Al_2O_3, and Al, in order of decreasing apparent content. The AlN is the most prevalent component, although it appears to have grown in a nonuniform manner with the (002) reflection having the highest intensity rather than the (100). This has been observed by other researchers, particularly during vapor phase synthesis of AlN, where the grains can be synthesized as large flat hexagonal plates[3]. From the peak broadening in the X-ray diffraction pattern, it appears that nanocrystalline AlN can be synthesized through nitridation of nanocrystalline aluminum. The aluminum content is extremely low, probably less than 5% as estimated from X-ray peak intensities. The γ-Al_2O_3 is probably formed due to small oxygen leaks in the TGA system. The formation of Al_2O_3 from Al corresponds to a weight gain of 189% so that partial oxidation of aluminum could result in a fortuitous weight gain. In this case, however, the presence of a large amount of AlN and smaller amounts of γ-Al_2O_3 and Al as determined by powder X-ray diffraction suggests that the primary source of the weight gain was aluminum nitridation and the γ-Al_2O_3 is due to small oxygen leaks in the TGA and possibly some crystallization of surface oxides created from exposure to air. Every effort will be made to minimize the oxygen contamination within the TGA, however the sample must be exposed to air during loading into the TGA so some oxygen will always be incorporated into the samples.

The observed low-temperature nitridation of the nanocrystalline materials over the bulk aluminum could be due to two possibilities. The first possibility is that the nanocrystalline aluminum only involves short diffusion distances so that the nitridation kinetics of the smaller particles reach completion significantly sooner than larger particles. The second possibility is that the nanocrystalline aluminum has greater surface reactivity, enabling a higher fraction of nitrogen to readily react with the aluminum. Both of these possibilities will be investigated in detail by nitriding aluminum of different

particle sizes and exposing the aluminum nanoparticles for different periods of time prior to nitridation.

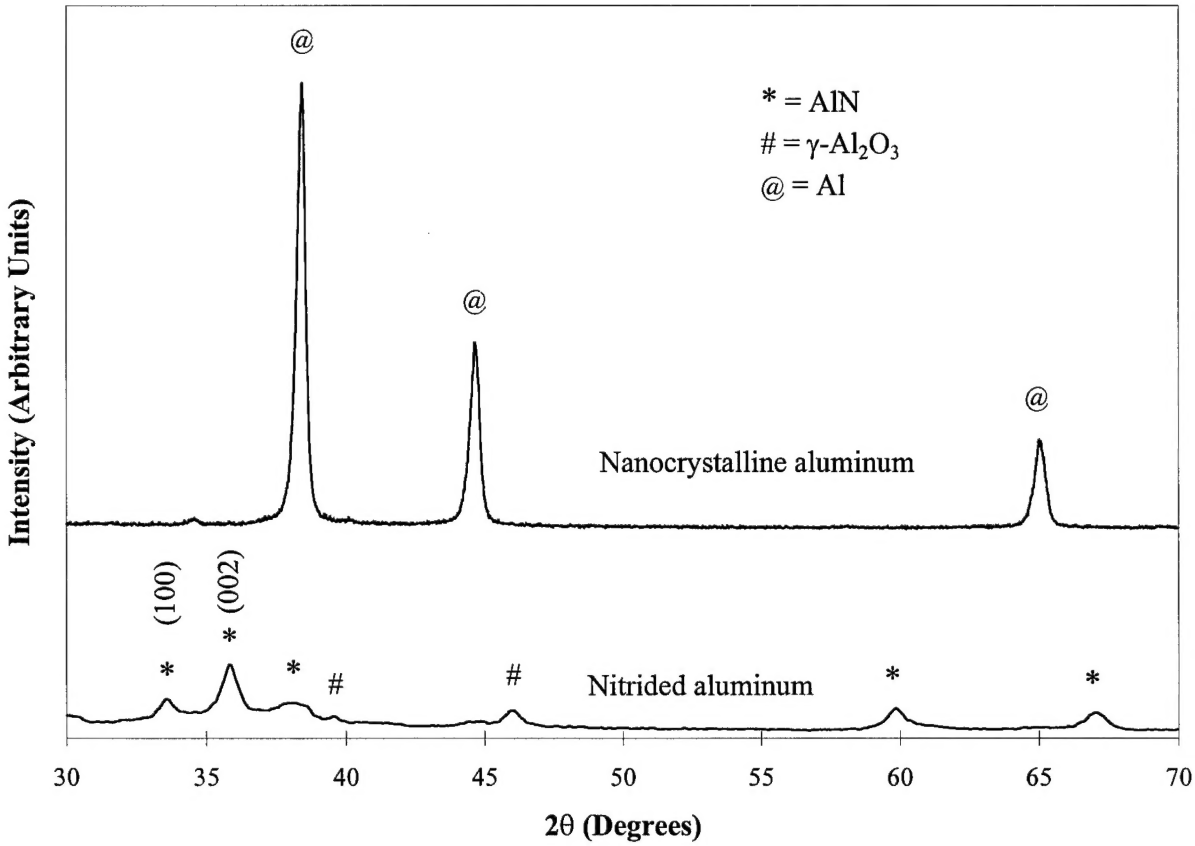

Figure 2. Powder X-ray diffraction patterns of nanocrystalline aluminum starting powder and nitrided product.

Future Work

In order to make large quantities of high-purity nanocrystalline AlN, a quartz nitridation reactor, which can be brought into the glove box for sample loading and unloading, will need to be constructed. This reactor will allow us to treat the material under air-free conditions and will also give us the flexibility to use ammonia to nitride the aluminum. Ammonia offers several advantages including a lower dissociation energy and a purification effect by reacting with any carbon or oxygen impurities to form CH_4 or H_2O. A more complete analysis of the nitridation kinetics of nanocrystalline aluminum is currently underway, as are experiments to produce pure nanocrystalline AlN directly within the forced flow reactor through the use of nitrogen microwave plasma.

[1] Panchula, M.L. and Ying, J.Y., M.I.T., unpublished results.

[2] Chang, A-J., Rhee, S-W., and Baik, S., "Kinetics and Mechanisms for Nitridation of Floating Aluminum Powder" *J. Am. Ceram. Soc.*, **78** [1] 33-40, (1995).

[3] Nickel, K.G., Riedel, R., and Petzow, G., "Thermodynamic and Experimental Study of High-Purity Aluminum Nitride Formation from Aluminum Chloride by Chemical Vapor Deposition" *J. Am. Ceram. Soc.*, **72** [10] 1804-10, (1989).